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Procedia Chemistry 19 (2016) 993 – 998

Procedia Chemistry

5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Synthesis of tin oxide nanostructures using hydrothermal method and optimization of its crystal size by using statistical design of experiment

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Abstract

This paper studies the effects of varying hydrothermal synthesis conditions (precursor concentration, reaction temperature and reaction duration) on the crystallite size of as-prepared tin oxide (SnO_2) nanostructures.The level of sensitivity of the synthesis parameters towards response and the optimization of the response were determined by applying statistical design of experiment (DOE). Based on cube plot, it can be summarized that the nanostructures with smallest crystal size (7.88 nm) can be obtained when precursor concentration was 0.16 M, treatment temperature was 120 °C with12 hour reaction time. On the other hand, the largest crystal size (18.41 nm)can be obtained at temperature of 180 °C using 0.12 M and 12 hour reaction time. From perturbation analysis with DOE, it was found that reaction temperature gave the most significant effect to the crystal size of SnO_2 nanostructures.

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: SnO_2 nanostructures; hydrothermal synthesis; crystal size.

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Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia
doi:10.1016/j.proche.2016.03.148

1. Introduction

SnO_2 nanostructures (NSs) have shown good sensing properties toward ethylene (C_2H_4), ethanol (C_2H_5OH), and CO gas due to wide band gap n-type semiconductor, leading to low electrical resistance and better electrical conductivity for gas sensing properties[1,2,3,4]. The sensitivity of metal oxide gas sensors are greatly depended on synthesis techniques, morphology, crystal structure, and grain size of the NSs[5]. According to Huang and Wan[6], small crystal size of metal oxide NSs can improve the sensitivity of the gas sensor because nanosized grains are almost depleted of carriers and have poor conductivity in air compared to micron sized grains. Thus, when nanosized grains are exposed to target gas, more charge carriers release from their trapped states to the conductance band, hence resulting in greater conductance changes than microsized grains.Understanding the factors controlling the crystal size of nanocrystalline SnO_2as well as the optimum synthesis parameters for producing a good crystalline structure of SnO_2 is very important. Hence, the powerful technique of statistical design of experiment was utilized to fine tune the variables involved in hydrothermal synthesis. The variables investigated in this study were reactant concentration, treatment temperature and reaction time.

2. Experimental

SnO_2 NSs were synthesized *via* hydrothermal method. Synthesis parameters such as precursor concentration, temperature, pH level and treatment duration in hydrothermal synthesis greatly influence the morphology and the crystal size of the synthesized products. In this process, the desired amount of $SnCl_4.5H_2O$ (0.12 M and 0.16 M) was mixed with 1:1 weight ratio of ethanol and distilled water. For enhancing the reactivity and homogeneity of the solutions, a magnetic stirrer was used and the solution was mixed for 10 minutes. During stirring, NaOH was slowly added until a pH 13 was reached. The mixture was stirred for 10 minutes and then transferred into a 50 ml Teflon-linked autoclave. The autoclave was placed in an oven under different reaction temperatures (120°C and 180 °C). After designated period of time (12 and 24 hours), the reactor was cooled to room temperature. The resulting solid product was filtered and washed several times with distilled water and ethanol, and with a final drying at 100°C in an oven. The formations of SnO_2 NSs were confirmed using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction spectroscopy (XRD). From XRD results, the crystal sizes of SnO_2 NSs were calculated using Scherrer equation and were analyzed using 2^k full factorial of DOE with three variables. All eight runs with different hydrothermal synthesis conditions are shown in Table 1.

3. Result and discussion

The results of crystal size calculations from XRD are presented in Table 1. Table 1 also list the DOE variables used in this study with 8 experimental run. The crystal structure and the crystal size of the as-prepared SnO_2 NSs were obtained from XRD analysis (Figure 1). The peaks at 2Θ values for SnO_2 were 26.6°, 33.8°, 37.9°, 51.7°, 54.8°, 57.5°, 61.9°, 64.5°, 65.9°, 71.0° and 78.7°. These peaks were be associated with the crystallographic planes of (1 1 0), (0 1 1), (0 2 0), (1 2 1), (2 2 0), (0 0 2), (1 3 0), (1 1 2), (0 3 1), (0 2 2) and (2 3 1), respectively. All diffraction lines match closely to the tetragonal rutile phase (ICSD #98-005-8477). From Figure 1, it should be noted that the SnO_2 NSs for Run 6 have much broader diffraction peaks and lower relative intensity than SnO_2 NSs for Run 8. Sample designated Run 6 was synthesized at lower temperature (120°C) which produced SnO_2 NSs that had much smaller crystallite size and lower crystallinity than Run 8 (180°C). Moreover, a sharper and higher relative intensity peaks at higher reaction temperature was attributed to highly crystallinity of SnO_2 NSs as the degree of crystallinity increase with reaction temperature[7]. The crystal size of NSs prepared by hydrothermal was obtained by using Scherrer equation (1) where K is Scherrer constant (0.89), λ is wavelength of Cu-K_α radiation (1.5406 Å), Θ is Bragg angle, FWHM is full width at half maximum and s is the instrumental broadening (0.0)[8].

Figure 2 presents the SEM images of the NSs with the smallest and the largest crystal size. The smallest crystal size was obtained when all three variables (precursor concentration, reaction temperature and reaction duration) were at their lowest levels (Run 1). This condition corresponded to a precursor concentration of 0.16 M, reaction temperature of 120°C with 12 hour reaction time. On the other hand, the largest crystal size was obtained when

precursor concentration and treatment duration were at their lowest levels and treatment temperature at highest level (Run 3). This conditions was achieved when precursor concentration was 0.16 M, reaction temperature was 180 °C at 12 hour reaction time. From analysis of variance (ANOVA) with DOE, standard deviation and R-squared values were 0.65 and 0.99 respectively which implied that the model is in a good agreement with experimental data. Crystal size can be expressed mathematically in equation (2) given by DOE analysis. The equations variables are listed in Table 1.

$$\text{Crystallite size, } D_p = \frac{180}{\pi} \frac{K\lambda}{\cos\theta\sqrt{FWHM^2 - s^2}} \quad (1)$$

$$\text{Crystal size} = 11.94 - 0.8*A + 2.54*B - 0.62*C - 1.95*B*C + 0.57*A*B*C \quad (2)$$

Table 1: Experimental run of full factorial design using 3 variables

Run	$SnCl_4.5H_2O$ Concentration (M) A	Temperature (°C) B	Time (Hour) C	Crystal size (nm)
1	-	-	-	7.88
2	+	-	-	8.25
3	-	+	-	18.6
4	+	+	-	15.48
5	-	-	+	11.91
6	+	-	+	9.56
7	-	+	+	12.55
8	+	+	+	11.25
	+ highest value	- Lowest value		

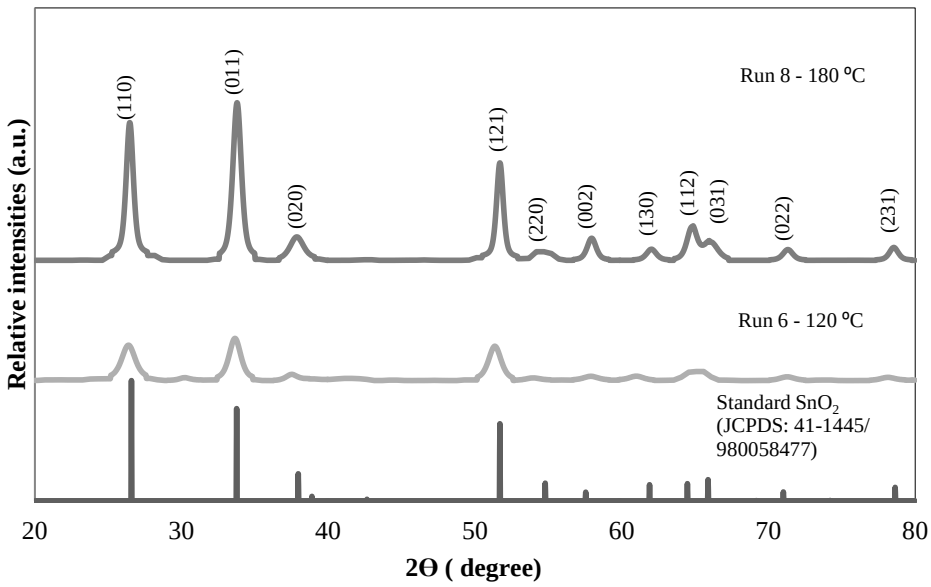

Figure 1: XRD spectra of NSs synthesized with 0.16 M of $SnCl_4.5H_2O$ and 24 h treatment duration with different temperatures

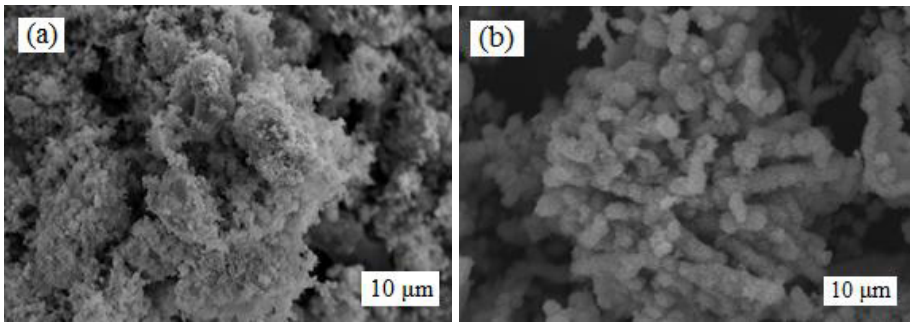

Figure 2: SEM images of NSs with the smallest and the largest crystal size. (a) Run 1 and (b) Run 3

Based on the predicted versus actual data plot (Figure 3a), it shows a good correlation between the model's predicted and experimental results. From the perturbation plot (Figure 3b), crystal size of SnO_2 NSs was mostly affected by hydrothermal temperature followed by $SnCl_4.5H_2O$ molar concentration and treatment duration. The positive gradient of variable B indicated that the crystal size increased with increasing temperature. However, the negative gradient for variables A and C implied an inverse relationship between these variables with crystal size. Low concentration of precursor reactants caused the reaction rate and the nucleation process to become slow which resulted in a broad size distribution of the SnO_2 nanocrystallites[9]. In addition, the probability that growth units combined into crystal plane was also significant[10]. Unlike temperature and precursor concentration variables, reaction time (C) had no significant effect on the crystallite size of the SnO_2 formation as shown in the perturbation plot.

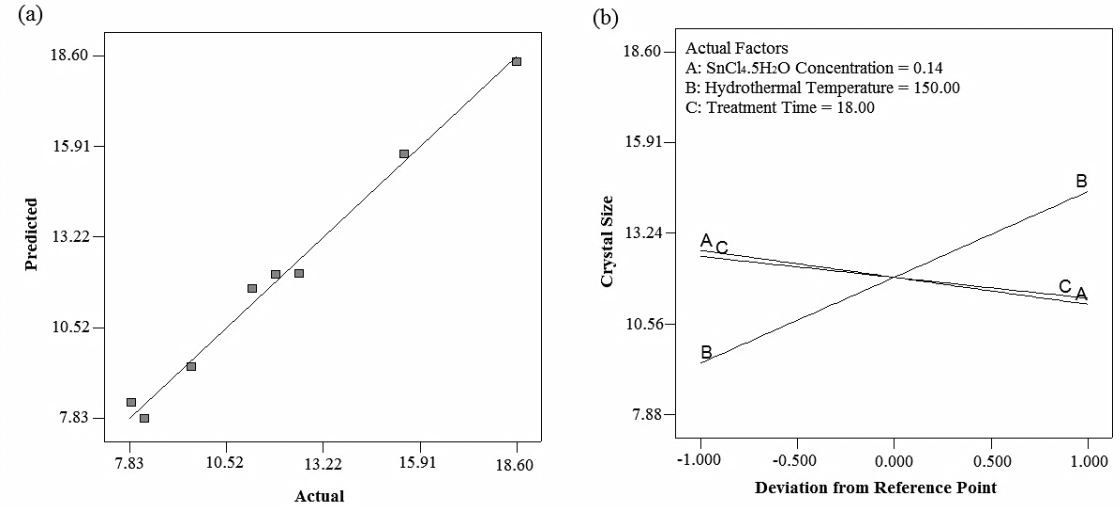

Figure 3: (a) Graph predicted vs. actual values. (b) Perturbation plot for SnO_2 NSs crystal size

On the other hand, interactive relationship between two significant factors (temperature and precursor concentration) and its response can be observed in Figure 4(a). From Figure 4(a), it was shown that at fixed reaction time, the crystal size decreased with decreasing temperature. According to Sui et al.[11], well crystallized NSs occurred at higher temperatures due to higher surface energy. The reaction temperature affects not only the reaction rate, but also the nucleation and growth rates of particles. Increasing the reaction temperature enhances the diffusion, nucleation and growth rates. Hence, highly crystalline and larger crystallite size of SnO_2 nanoparticles are formed at these conditions[11].

The optimization of crystal size can be determined by using the cube plot in DOE analysis. Figure 4(b) presents the cube plot for crystal size ranged from 7 to 18 nm in terms of process parameters. The smallest crystal size (7.83 nm) can be produced at lowest level of temperature and treatment time and highest level of $SnCl_4.5H_2O$ concentration. In contrast, the largest crystal size (18.41 nm) can be obtained at lowest level of reaction time and precursor concentration with the highest temperature. Furthermore, the contour and cube plot confirms that the temperature had the most significant effect on SnO_2 NSs crystal size. In comparison to other variables investigated, formation of SnO_2 crystal size lower than 12 nm was only possible at 120°C. The smaller crystallite size will play an important role in enhancing electrical conductivity and gas sensing sensitivity[1].

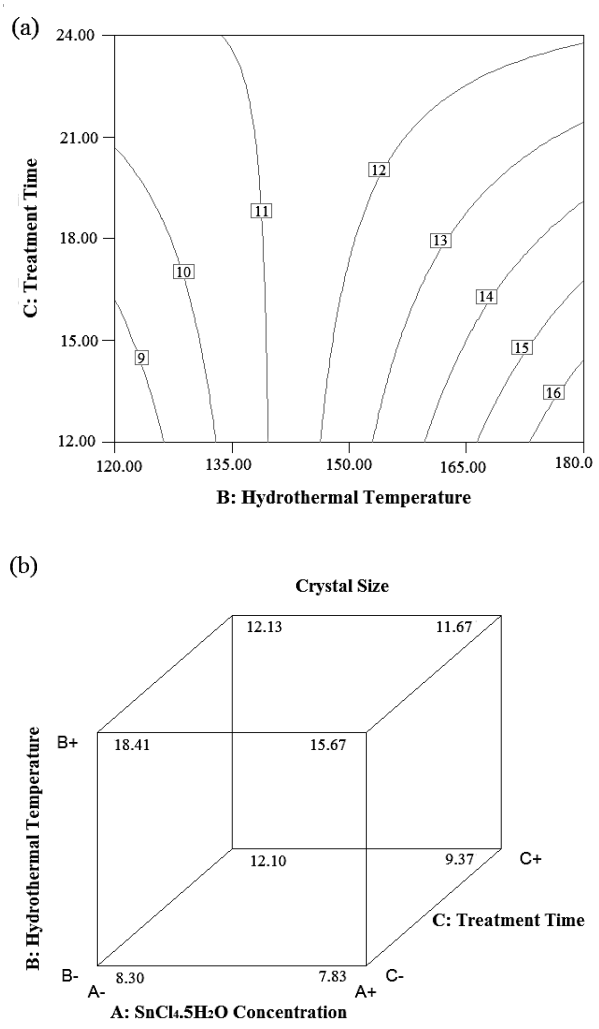

Figure 4: (a) Contour plot of crystal size as a function of factors B and C using 0.14 M precursor concentration. (b) Cube plot of the interaction of factors A, B, and C with respect to crystal size

4. Conclusion

The synthesis of SnO_2 NSs using hydrothermal technique was successfully achieved by varying synthesis conditions. Statistical design of experiment based on full factorial model using three variables (precursor concentration, temperature and treatment time) was used to study the effect of each variable with crystal size of as-synthesized SnO_2 NSs. It was noticed that temperature had most significant effect on crystal size followed by precursor concentration and reaction time. Based on the contour and cube plot, the smallest crystal size (~7 nm) was obtained when $SnCl_4.5H_2O$ concentration was 0.16 M at 120 °C with 12 hour reaction time. On the other hand, the largest crystal size (~18 nm) was achieved when 0.12 M of precursor concentration was used at 180 °C with 12 hour of reaction time. DOE analysis of the crystallite size effect with respect to the above variables showed that it can identify important factors that governed reaction mechanism in forming NSs.

Acknowledgements

The author is grateful to School of Chemical Science, Nanofabrication and Functional Materials Lab, School of Mechanical Engineering and School of Materials & Mineral Resources Engineering, USM, for providing the facilities to carry out the research. The research is funded by USM short term grant 304/PKimia/6313032 and FRGS 203/PBahan/6071261.

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